



Review

Advances in catalytic oxidation of organic pollutants – Prospects for thorough mineralization by natural clay catalysts



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ABSTRACT

This review is devoted to oxidative water treatments, with emphasis on catalytic ozonation. The approach tackled herein resides in exposing a wide variety of oxidative treatments attempts as a basis for summarizing the main findings that allow envisaging improvements aiming towards total mineralization of organic pollutants. Comparison between specific operating conditions for specific pollutant-catalyst-oxidizing systems is quite difficult, and is not targeted in the present work. However, when deeply and judiciously analyzed, such a comparison allows demonstrating that, except for some works, most of these attempts seldom took into accounts basic requirements such as the parameter interactions, the role of cation mobility around a solid surface, if any, the multiple pollutant-catalyst-oxidizing species interactions and the significant contribution of adsorption, etc. Otherwise, how to explain that many experiments are still conducted with unsuitable catalysts under totally inadequate operating conditions? A better understanding of the essential requirements for a catalyst to achieve total mineralization of any organic molecules is the main objective of this work.

The data summarized herein allow devoting a special interest to ozone, which is a powerful oxidizing agent and probably the most easily handleable, in spite of its low solubility in water. The use of catalysts is an ultimate strategy to improve the ozonation performance, by reducing the chemical oxygen demand (COD), even until total disappearance. However, solid catalysts, more particularly those developing high specific surface areas, such as silicates, aluminosilicates, zeolites, pseudozeolites, and clay minerals and derivatives are expected to display appreciable performances in ozonation. The latest findings show strong dependency of their catalytic activity on the chemical and physical characteristics of their surface, their concentration in the liquid media, the pH level of the reaction mixture and other parameters. The effects of these factors will be systematically examined in this review paper. The state-of-the-art in the catalytic ozonation of organic pollutants may be useful to understand the contribution of both surface and bulk ozonation reaction in the vicinity of the surface of a solid catalyst, and more particularly the role of the catalytic agent and its mobility near the solid surface. A rigorous data synthesis, made available in the present paper, allows understanding the ozone scavenging by the very species present in water, and correlating the highest effectiveness of ozone in the presence of optimum catalyst concentration at optimum pH. This supposes strong interactions between the main factors, which remain to be elucidated for each type of catalyst.

The structure of this review makes emphasis on montmorillonite, which exhibits most of the required properties for effective ozonation catalysts. These are common features of natural clay minerals and zeolites, which appear as interesting candidates for large-scale water treatments, targeting complete mineralization of organic pollutants without generating persistent toxins.

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1. Introduction

Water pollution remains a major issue to be addressed by improving wastewater treatments not only from conventional industries but also for novel eco-designed technologies to be implemented. Among the different water treatment methods tested so far, oxidative techniques are undoubtedly the most promising routes when total mineralization of organic pollutants is targeted. There exists a wide variety of oxidative techniques such as Fenton and photo-Fenton processes, ozonation and catalytic ozonation, photocatalysis in the presence of hydrogen peroxide with, for example, titanium dioxide, radiolysis, electrochemical oxidations and various combinations of some of these procedures. All these techniques have more or less efficiency, but their common feature resides in the unavoidable formation of harmful by-products in the case of incomplete decomposition of the organic substrates.

Among these, catalytic ozonation is one of the most effective and eco-friendly wastewater treatments [1]. Ozone is a powerful oxidizing agent that may lead to complete mineralization of organic $C_xH_yO_z$ compounds into carbon dioxide under specific operating conditions [2,3], with sulfate and nitrate anions when S and N atoms are also present. This allows envisaging potential applications in industrial processes [4]. Nonetheless, ozone is characterized by a short lifetime and low solubility in aqueous media. These are major drawbacks that reduce considerably the contact time in water and interaction with the organic substrates to be decomposed. Ozone alone often results in incomplete degradation of the organic substrate [4], and, paradoxically, even acts as a potential source of toxic intermediates. Significant improvements can be brought by using solid catalysts, which are also supposed to favor adsorption, prolonging thereby the contact time in the liquid media. Solid catalysts displaying high specific surface area could be of great benefit for wastewater treatments aiming to total decomposition of organic contaminants without generating persistent by-products (*Scheme 1*). This could be regarded as an interesting route to explore.

Nowadays, ozonation methods are routine technologies in wastewater treatments, more particularly in some European countries [5,6]. Ozone has promising perspectives in wastewater treatments, because it can be easily produced from air by means of compact and small volume devices that operate at ambient pressure and temperature [7]. According to numerous references, in small concentration not exceeding 5–50 ppm for exposure times ranging from 30 to 60 min, ozone is not hazardous for human health and can be simply handled. In addition, it can readily decompose into harmless compounds (oxygen and water). Because, different ozone dosages are involved for treating different types of wastewater,

optimum usage of ozone requires a minimum knowledge about the origin and the emission sources of the wastewaters to be treated. This implies that effective oxidative treatment needs sufficient data on the chemical composition of the effluents and the nature of the organic pollutants to be decomposed.

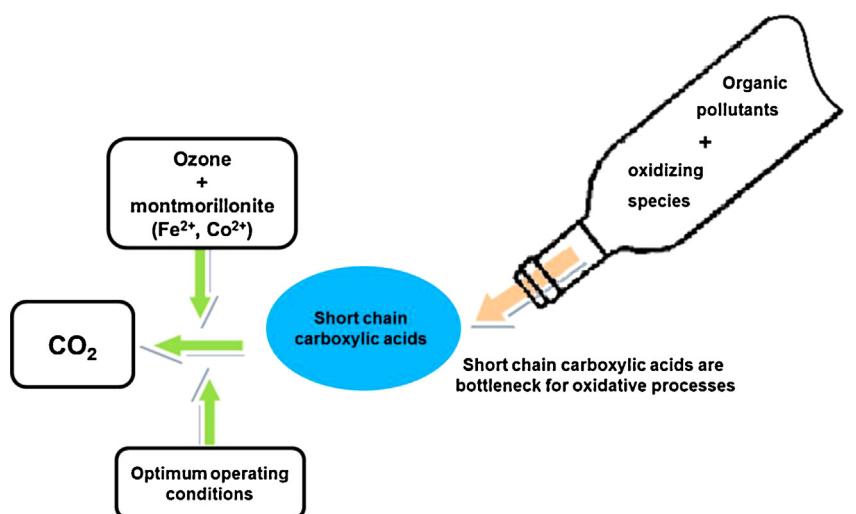
A wide variety of hazardous compounds that may affect human health through as neurological disorders, cardiovascular and even diarrheal diseases [8] can be eliminated by wet oxidative treatments at ambient temperature. When optimized, oxidative techniques do not generate harmful products, unlike, for instance, incineration methods that produce toxic emissions [9–14]. Wet oxidative treatments are confronted to a hard challenge, inasmuch as the maximum permissible concentration of some persistent organic compounds and dyestuffs in some wastewaters is much less than 1 ppm, while the outlet concentration from chemical plants is often several times higher than the allowed threshold [15–18]. Even other attempts through biological and physical water decontamination from organic pollutants turned out to be unsatisfactory as compared to advanced oxidative processes (AOPs) [19–23].

2. Water pollution by organic compounds

Wastewaters contain a wide variety of chemical compounds such as organic pollutants, eutrophication agents (nitrates, phosphates), metal cations and others (*Scheme 2*). Such a diversity requires different approaches in wastewater treatments, and a special interest is focused herein to organic pollutants. Their common features reside in their high reactivity toward oxidizing agents, more particularly to ozone, regardless to their different physico-chemical nature.

Major organic pollutants arise from chemical and pharmaceutical industries, food technologies, oil refineries, petrochemical plants, dye and textiles manufacturing units, agro-industrial activities, and others. Petrochemical wastewaters often contain oils and greases, phenols, aromatics and chlorinated organic compounds such as dioxins. Paper and pulp mills, sugar mills and leather tanneries are other important emission sources of organic pollutants [3,8]. Organic wastes originating from industrial and urban sewages, also contain hazardous compounds such as aromatic hydrocarbons, petroleum products, halogenated solvents, herbicides like 2,4-dichlorophenoxyacetic acid, detergents, phenols and derivatives, antibiotics, estrogens, contraceptives, and require treatments before being released in soils, streams, rivers and seas [9–15].

Phenolic compounds are an important family of wastewater polluting agents. They usually arise from chemical industries for the manufacture of pesticides, pharmaceuticals, synthetic dyes

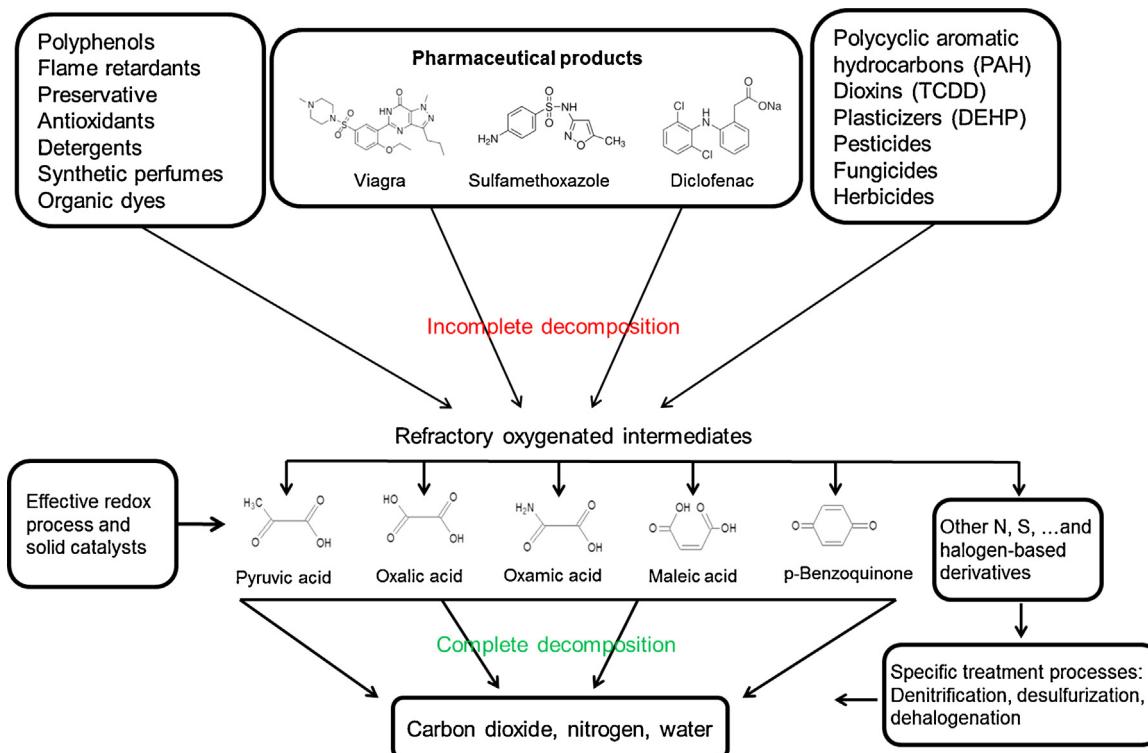
**Scheme 1.** Effective strategy for total mineralization of organic contaminants.

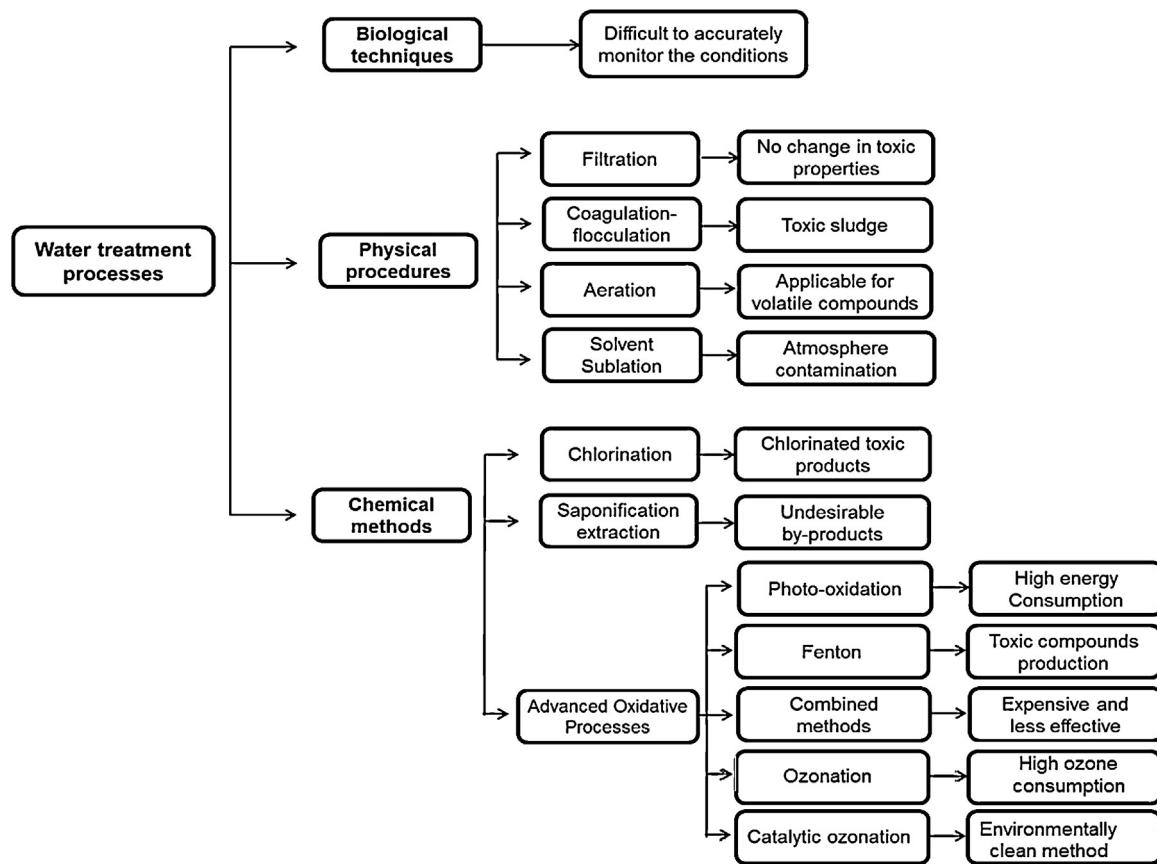
(Adapted from Ref. 60).

[12], fuel additives [13], and food-processing industries, more particularly from olive oil and wine producing plants around the Mediterranean [14,16]. They may also originate from incomplete oxidative treatments of a wide variety of organic pollutants.

Organic dyes and azo derivatives, in particular, are also released in wastewaters, most of them showing carcinogenic, mutagenic and allergenic effects for living organisms. Such compounds are difficult to remove through physical treatment methods, and only oxidative decolorization of the corresponding wastewaters can be considered [17]. However, care should be taken in the case of incomplete oxidation, because traces of hazardous derivatives may be generated. The latter are usually regarded as being persistent organic pollutants (POP).

Polyaromatic hydrocarbons (PAHs) are a class of high molecular weight organic compounds with three or more phenyl rings, including bicyclic compounds such as naphthalene and biphenyl [18]. Such compounds are regarded as being particularly toxic, and unless thermally decomposed into heavy asphalt-derived compounds, they usually generate phenolic compounds upon oxidative treatments. That is being said, as previously stated, each organic pollutant family requires specific elimination methods. The latter should be judiciously chosen by imposing minimum traces of residual organic pollutants and derivatives, if any, as the main criterion. Obviously, this supposes that previous constraints related to energy consumption and CO_2 emission considerations are satisfactorily taken into accounts.

**Scheme 2.** Main sources of organic contaminants and oxidative degradation strategy.



Scheme 3. Main approaches for organic pollutants elimination.

3. Removal of suspended and dissolved organic compounds

The dispersion state of organic pollutants in the liquid media is a key-factor in applying adequate elimination techniques for a given family of organic compounds. For instance, suspended organic compounds can be conveniently separated from wastewater by different scale filtrations and settling, while emulsified or dissolved organic compounds may be removed either by precipitation, solvent extraction or through oxidative methods (Scheme 3). According to the type of organic contaminants to be removed, physical procedures involving adsorption, coagulation and (or) flocculation, or even biological procedures may be applied for wastewater remediation.

3.1. Conventional techniques

Biological treatment using micro-organisms has long been used to eliminate eutrophication agents and pollutants. Fungal and bacterial degradation of organic compounds is known as bioremediation. Fungi were already found to convert pesticides into nontoxic derivatives, which are further degraded by bacteria [19]. Reportedly, *Oxalobacter formigenes*, an anaerobic bacterium isolated from human feces, has the ability to degrade oxalic acid [20], and appreciable mineralization levels were achieved using *Coniothyrium minitans* fungus or brown rot fungus [21,22]. In spite of these performances, bioremediation processes are often pH-dependent and fairly difficult to be accurately monitored. Appreciable fluctuations in their activity due to frequent contaminations with other competitive micro-organisms may affect the process efficiency.

In physical procedures, dispersed contaminants in both liquid (solution or emulsion) and solid state (suspension) are separated

from the liquid media without changes in chemical structure. Such methods are usually applied for removing highly polluted wastewater, and have almost no efficiency when dealing with complete purification into drinking water. When applicable, microfiltration is undoubtedly one of the most important physical water treatments, which involves separation via filtration of small particles [23]. This method uses entangled wires made of stainless steel or polymers as filters with aperture size of only 60–70 µm. Other similar procedures developed so far, utilize membranes and other separating systems. In the case of very fine particles, a previous coagulation-flocculation process is employed in order to increase the particle size through the formation of flocs.

Coagulation, alone or combined with other methods, is usually employed to alter colloidal states by modifying the surface charges of the suspended particles. An almost similar process is involved with the emulsion of liquid micro-droplets. For this purpose, coagulating agents, such as aluminum sulphate [$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$], FeCl_3 or FeSO_4 are commonly employed [23,24]. Devoid of their solvation layer, these agents can adhere to each other into bulkier and heavier aggregates (flocs). The latter are prone to settling steps, and the residual suspension is removed through filtration of the supernatant [25,26].

Pollutants capture through adsorption on solid surfaces is the most commonly used physical technique for removing dissolved compounds. However, this technique should be limited to wastewater weakly loaded in contaminants and as long as adsorbent saturation is not reached. The adsorbent effectiveness is directly related to the extent of the surface area available for interaction with the contaminating molecules. A classical adsorbent, with high affinity toward organic compounds, is undoubtedly porous carbon in all its structural forms (activated carbon, graphene, fullerenes, carbon nanotubes, etc.) [27]. Nanostructured carbons can display

surface areas of $1000\text{ m}^2\text{ g}^{-1}$ and even beyond. Activated carbon is the most affordable carbon-based material from the production cost viewpoint, and can act as an effective adsorbent for a wide variety of organic substrates [15,25,28–30].

Solvent sublation or commonly “solvent extraction” is a conventional treatment for highly polluted aqueous wastewaters. In this separation technique, the dissolved organic compound is transferred and concentrated at the top of a column filled with an organic solvent by means of ascendant micro bubbles of air. This method turned out to be more effective than the aeration methods, because it prevents the organic contaminant to re-disperse into the aqueous phase. In addition, unlike aeration methods, solvent sublation can also eliminate non-volatile pollutants [31]. Evaporation of the organic contaminant into the air stream during the aeration treatment can be achieved by increasing the liquid–gas interface. For this purpose, bubbling large amounts of air through the wastewater bulk causes air and water to disperse into a mixture of fine bubbles and very small droplets [32–34]. The efficiency of such physical methods is however limited by the transfer velocity of the contaminant through the liquid–liquid (sublation) or liquid–gas interface (aeration). The main drawback of such a water treatment technique is the use of organic solvents, which unavoidably results in traces of organic molecules. That is why, even the most performing devices cannot produce total elimination of the organic substrates from treated wastewaters.

Another route involves the use of chemical methods, i.e., the decomposition of organic compounds into products with different chemical structures. An essential requirement for such wastewaters treatments resides in achieving weakly endothermic chemical reactions. The latter should use powerful oxidizing or reducing agents in order to avoid heating and the production of residual amounts of harmful products and hazardous derivatives. Here, a special interest is devoted to those treatment processes that do not involve fossil energy consumption and greenhouse gas emissions. Such degradation reactions should also show fast kinetics and high conversion yields. When such requirements are not fully satisfied, improvements can be brought by using suitable catalytic systems, but, in most cases, the operating conditions have to be optimized in correlation with the catalyst features. For instance, polychlorinated biphenyls (PCBs) are an important kind of persistent organic pollutants, which can be degraded by saponification, but the reaction is more efficient upon heating [35]. Polyaromatic hydrocarbons (PAHs) may also be removed by saponification, but the reaction mixture was found to still contain undesirable by-products even under reflux at 95°C [36]. For such decomposition processes, the needs for heating are major shortcomings, which limit their applications for large-scale batches.

Theoretically, the mere presence of carbon atoms in their structure makes that all organic molecules can react with oxygen and oxidizing agents. The most commonly employed oxidizing agents are permanganate and hypochlorite anions, hydrogen peroxide and ozone. A wide variety of oxidative decomposition processes has been developed until now, among which chlorination has even been employed in industrial facilities for wastewater treatments. Nevertheless, such techniques are progressively losing interest, because of the unavoidable formation of chlorinated by-products.

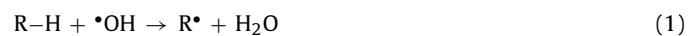
3.2. Oxidative processes for total mineralization

Oxidative procedures targeting total mineralization of organic pollutants into harmless final products, more particularly the so-called advanced oxidative processes (AOP) have particularly attracted attention. The most important AOPs may be classified as follows [28]:

- (a) Fenton processes (using $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ combination, known as the Fenton's reagent);
- (b) Ozonation –peroxidation combination ($\text{O}_3/\text{H}_2\text{O}_2$);
- (c) Photo-oxidation processes: (O_3/UV ; $\text{H}_2\text{O}_2/\text{UV}$; $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$);
- (d) Catalytic photo-ozonation: (catalyst/ O_3/UV);
- (e) Catalytic ozonation: catalyst/ O_3 .

Regarded as being environmentally clean treatments of wastewaters, they are still prone to intensive investigations. When applied to oxygenated organic contaminants that do not contain heteroatoms such as sulfur or nitrogen, effective AOPs should ideally only generate CO_2 and H_2O as the final products. In most AOPs, the main oxidizing agent is the hydroxyl free radical ($\cdot\text{OH}$), more particularly in alkaline media. This radical is even more reactive than chlorine, permanganate and hydrogen peroxide, being a non-selective oxidizing species that readily and rapidly reacts with a wide variety of organic substrates [9,13,22].

Most AOPs involve a direct attack of hydroxyl radicals on the organic molecules yielding organic radicals and water (Reaction (1)) [37]:



In this reaction, $\text{C}=\text{C}$ compounds are more reactive toward $\cdot\text{OH}$ radical attack than saturated molecules, and the reactivity toward oxidative species decreases with decreasing molecular weight and increasing oxidation level. This explains why partial oxidation of organic molecules generates smaller size derivatives, usually oxalic acid and short chain intermediates, which display lower reactivity toward oxidation than their parent molecule. The latter usually accumulate as the final products, because they are known to be quite refractory even to the most reactive oxidizing species. Catalytic oxidation of organic pollutants may produce total mineralization into CO_2 and water, but only under optimum amounts of catalyst and oxidizing agent, pH and concentrations of the organic substrate [38]. Catalytic oxidation of organic molecules containing sulfur, nitrogen and (or) other heteroatoms is expected to generate also nitrate and sulphate anions.

At ambient temperature and pressure, oxidative processes generate sufficient $\cdot\text{OH}$ radicals to oxidize the major part of the organic compounds present in polluted water [37,39–41], but such radicals show limited efficiency, more particularly in flow water treatment, due to their extremely short lifetime.

One of the most conventional oxidative methods is the Fenton process [12], which displays its highest efficiency around pH 3, due to the preponderance of Fe^{2+} cation at the expense of its ferric counterpart (Fe^{3+}). Here, the $[\text{Fe}^{2+}/\text{H}_2\text{O}_2]$ ratio, H_2O_2 concentration, temperature, initial concentration of the pollutant, and, more particularly pH are expected to play key roles. Increasing pH was found to be detrimental because it reduces the amount of Fe^{2+} cations via precipitation. This is expected to attenuate the conversion of hydrogen peroxide into $\cdot\text{OH}$ radicals (Reaction (2)) [42]:



The major shortcoming is that such a process may be a source of water contamination, because exhaustive $\cdot\text{OH}$ production requires appreciable Fe^{2+} concentrations of 50–80 ppm, while the maximum level allowed in treated wastewaters is only 2 ppm. Another drawback is that high Fe^{2+} concentrations require continuous pH adjustments that raise the operating costs in wastewater treatments [43]. Besides, the H_2O_2 amount should be rigorously monitored to avoid $\cdot\text{OH}$ radical scavenging even by hydrogen peroxide, resulting in less reactive species such as HO_2^\bullet (Reaction (3)) [3,15,44]:



Photo-catalytic oxidation of organic substrates was found to produce higher performances when using solid catalysts such as

TiO_2 in its anatase form, metal oxides and sulfides such as $\alpha\text{-Fe}_2\text{O}_3$, SrTiO_3 , WO_3 , ZnO , and ZnS [6]. A major requirement resides in the chemical stability of such catalysts under light exposure. However, light irradiation involves energy consumption and increased operating costs that impede their large-scale implementation, unless using solar light. For these reasons, the design of new oxidative methods, more particularly ozone-based AOPs, turns out to be attractive.

3.3. The state of the art about ozonation

Under optimum operating conditions, ozonation and its improved variants appear to be the most promising routes for wastewater treatment, even those containing complex organic molecules such as antibiotics, estrogens and other drugs. Nowadays, a wide variety of mini- and micro-devices are available for domestic purposes, and more particularly for drinking water. Ozonation is progressively becoming an almost unavoidable technique for quick water purification, notwithstanding the low solubility of ozone in water, which barely reaches 570 mg L^{-1} at 20°C [45] for pure ozone in the gas phase. This solubility dramatically drops down at lower ozone concentrations in the gas phase according to Henry's law. Ozone can be conveniently generated through an electrical discharge using pure oxygen or even air, with an average energy consumption of $8\text{--}17 \text{ kWh/kg}$ of ozone [46].

Molecular ozone is fairly unstable in water with a half-life time ranging from few seconds up to few minutes, according to the pH of the liquid media. Between pH 7 and 10, the typical half-life time of ozone varies from 15 up to 25 min. The ozone reactivity arises from its two forms of resonance structures (**Scheme 4**), which explains the high probability of different type of chemical reactions such as cycloaddition, electrophilic and nucleophilic attacks.

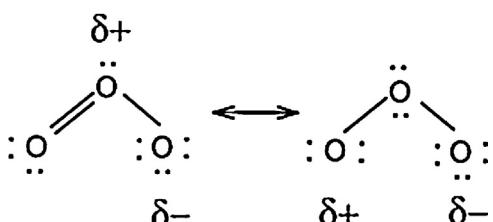
Ozone molecules exhibit redox potential of 2.07 V , which is supposed to induce sufficient reactivity to oxidize both organic and inorganic compounds [28], as supported by proton oxidation in water (Reaction (4)):



This scavenging effect of protons partially impedes direct interaction of ozone with both the substrate and catalyst, and explains somehow why excessively acidic media are detrimental for ozonation processes. In less acidic media, the mere presence of hydroxyl anions turns out to be rather beneficial, inasmuch as direct ozone attack on hydroxyl anions generates highly reactive $\cdot\text{OH}$ radicals (Reaction (5)):



$\cdot\text{OH}$ radical displays a higher oxidation potential (2.33 V) [28], and a rate of attack typically $10^6\text{--}10^9$ times faster as compared to molecular ozone [9]. Increasing alkalinity in the reaction mixture should be beneficial, but beyond a certain threshold level, in metal cation-catalyzed ozonation, the precipitation of catalytically active metal cations may take place. This indicates the occurrence of optimum pH. According to the mechanism pathways proposed so far,



Scheme 4. Ozone charge transition between two resonance structures.

molecular ozone behaves as a primary oxidant, and, once generated, the resulting $\cdot\text{OH}$ radicals act as secondary oxidizing agents [47]. Unavoidably, $\cdot\text{OH}$ radicals can even react with ozone, inducing a reciprocal annihilation of the oxidizing capacities of both species by generating much less reactive $\text{HO}_2\cdot$ radicals (Reaction (6)).



The latter may also react with ozone to form hydroxyl radicals (Reaction (7)), but to a lesser extent because of their relatively low reactivity. Since the concentration of ozone in aqueous media is limited by its low solubility, it clearly appears that excessive amount of hydroxyl radicals will enhance their detrimental scavenging effect on ozone molecules. Here care should be taken, because too alkaline pH's causes an increase in ozone decomposition into radicals with lower reactivity (Reaction (8)). Some of these radicals ($2\text{HO}_2\cdot$) may however behave as a valuable source for hydrogen peroxide (Reaction (9)).

These findings constitute the basic knowledge for improving ozonation processes. In a first step, to overcome the major drawback related to low ozone solubility, the contact time of ozone or the extent of the gas–liquid interface in the reaction mixture should be significantly increased. For this purpose, a series of engineering solutions have been developed, e.g., high bubble dispersion and the use of long tubular reactors. In such devices, the overall reaction rates were found to depend on both the transfer rates of ozone from the gas bubbles to the liquid and the reaction rates of ozone with the organic pollutants [48].

The low solubility of ozone in aqueous media has also stimulated research for developing chemical procedures, e.g., by using solid catalysts such as polymers and zeolites [49]. In this regard, fixed beds of porous glass or metals, or the use of solid catalysts that also act as adsorbents are also interesting routes that have been explored. So far, free transition metal ions and mixed oxides have shown interesting catalytic activity toward the ozonation of organic pollutants [50]. However, catalyst loss and water contamination with metal cations are the main shortcomings of such methods. The use of supported metal cations is a possible solution in this regard, but the chemical stability of the solid supports, more particularly in acidic media, should be an essential requirement for this purpose. In addition, metal cations should benefit of a certain mobility to be active, and ion-exchangers appear as promising supports, but metal losses by leaching due to pH fluctuations are still possible.

The frequency of the interactions occurring between ozone and the $\cdot\text{OH}$ radicals may also be prevented by operating in laminar flow processes. Microfluidic processes in tubular reactors with internal coating showing catalytic activity in ozonation may constitute an interesting route to explore. Investigations should be focused in this direction.

Ozonation has seldom been applied for large scale purposes, except in some special cases such as in the cleaning treatment of ship ballast waters. This came as an alternative to the negative impacts of chemical compounds used for this purpose in conventional treatments [51]. Here, total mineralization of refractory small molecules is an essential requirement to avoid sea water contamination, which can be achieved only through catalytic ozonation [15,52].

When used for decolorizing textile wastewaters, conventional ozonation involves high ozone consumption. The latter is almost 4 times lower by catalytic ozonation [53]. Under these conditions, ozone is usually injected at a concentration of $12.0 \pm 0.5 \text{ mg L}^{-1}$ in the feed gas and gas throughput of 1.0 L min^{-1}

[54]. In all possible applications, the electron density (ED) of the targeted molecules plays an important role on the electrophilic attack of ozone. As a general feature, increasing ED accounts for increasing reactivity toward ozone.

This dependence may be significantly influenced by the presence of a catalyst [7]. For phenolic compounds, for instance, the reactivity toward ozone is strongly dependent on the number, type and position of functional groups attached to the aromatic ring. It generally decreases with decreasing number of hydroxyls and increasing number of methoxy groups. Methoxylated compounds were found to show lower total oxidation rates than phenolic derivatives [16].

Ozonation produces only partial degradation of pesticides in coupled chemical and biological treatments [55]. This often results in the formation of hazardous intermediates [56]. For instance, when ozonized, phenolic compounds give rise to common derivatives such as resorcinol, catechol and hydroquinone, along with fumaric, maleic, glyoxylic, oxalic and formic acids [10]. Such derivatives usually exhibit weak reactivity toward oxidizing species, because of the presence of several oxygen atoms in their structures [57]. Antibiotics are typical organic pollutants in a wide variety of domestic and industrial wastewaters at sub-therapeutic concentrations. Seemingly, ozonation attempts at alkaline pH gave better performances than acidic media [58]. Nonetheless, pH fluctuations during the ozonation process may produce changes in the mechanism pathways, making the elimination of the organic contaminants difficult to be monitored [48,59]. Unless effective catalysts are used, drugs and estrogens released in the environment still remains a major issue to be addressed.

4. Catalytic ozonation

In surface catalysis, the overall rate of a physico-chemical process is governed by the contribution of different consecutive steps, and more particularly by the kinetic-controlling step [7]. Depending on the strength of the reagent-surface interaction, the ozonation process can involve physical or chemical adsorption. Too strong interaction of the reagents, intermediates or products leads to catalyst poisoning.

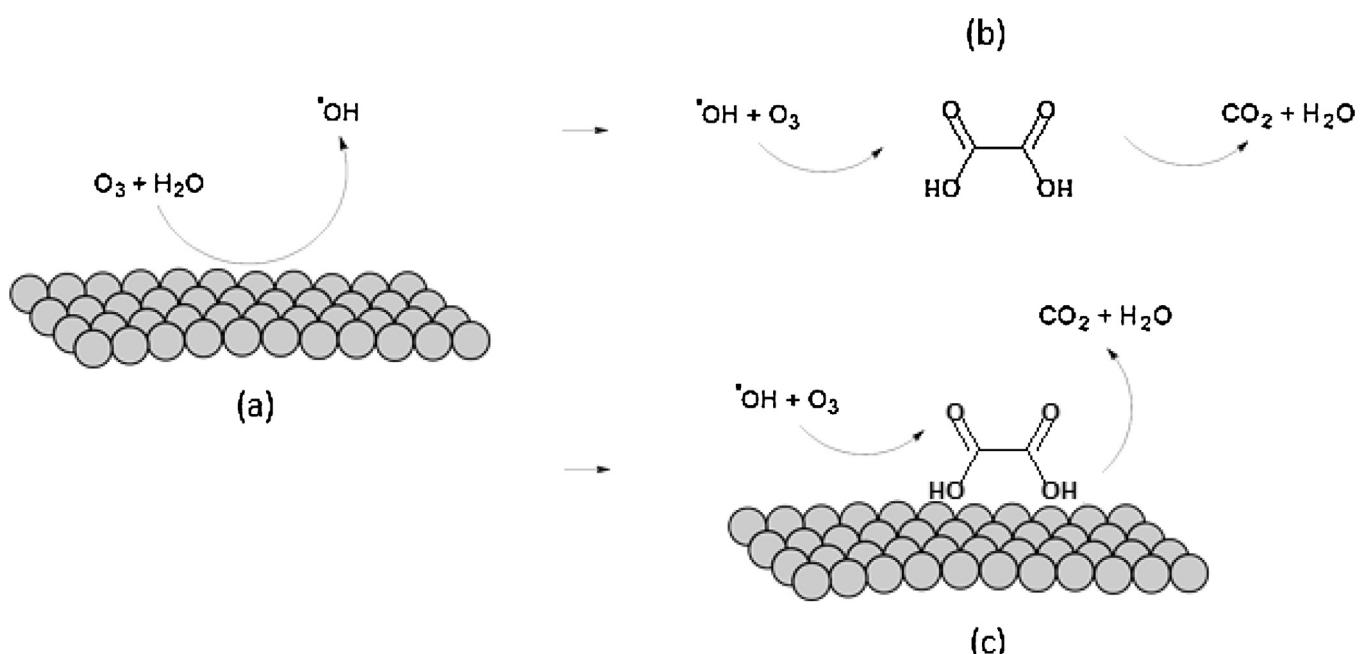
All ozonation methods proceed via heterogeneous processes, because it involves, at least, a surface reaction between a gas (ozone) and a liquid media containing the organic pollutants [28]. The latter may be dissolved or merely dispersed as an emulsion (if liquid) or a suspension (if solid). That is why, care should be taken when using abusively the terms "homogenous catalytic ozonation" [28]. The latter arise from an incorrect denotation that should be avoided as much as possible, whatever the catalyst physical state may be.

The first catalysts ever used in preliminary ozonation studies were dissolved metal cations. Until today, salt of transition metals such as Fe^{2+} , Fe^{3+} , Mo^{6+} , Mn^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+} , Ag^{+} , Cr^{3+} and Zn^{2+} are still used as catalysts for this purpose [5,59–61]. So far, bivalent cations, and more particularly Fe^{2+} ions, showed the highest catalytic performances [59,61]. In Fenton processes, Fe^{3+} cations are assumed to decompose H_2O_2 into oxygen and water without generating the targeted hydroxyl radicals [62]. In the ozonation process, a key step resides in the direct interaction between ozone and bivalent iron cations (Reaction (10)). This reaction is supposed to take place, giving rise to FeO^{2+} cations. The latter is now recognized as being the main precursors of hydroxyl radicals even in acidic media (Reaction (11)).



The formation of OH^- anions unavoidably induces pH increases and changes in the mechanism pathways [48,59]. This is expected to cause catalyst loss through metal cation precipitation, and to shift equilibrium toward an attenuation of Reaction (11). This is a major drawback that makes the implementation of large scale cation-catalyzed ozonation difficult to be achieved. Besides, the presence of metal cations in the treated wastewaters is another major issue to be addressed, and the use of insoluble solid catalyst appears as being more promising alternatives. Oxides of metals such as Cu, Mn, Co, Cr, V, Ti, Bi, and Zn in different oxidation states and supported or free metal particles such as (Ir, Pd, Pt, Rh, and Ru can be used for this purpose.

The use of solid or supported catalysts aims not only to overcome these shortcomings, but also to provide extended specific surface



Scheme 5. Interfacial radical generation (a) and radical action on oxalic acid in the bulk solution (b) and on the catalyst surface (c).

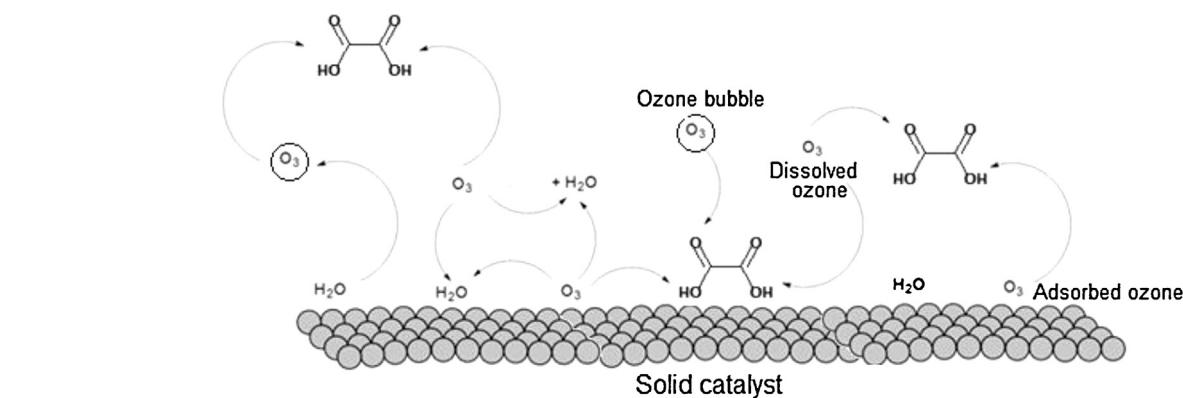
areas for improving the contribution of adsorption [6,48]. The latter will be more or less significant according to the acid-base properties of the solid surfaces. So far, a wide variety of solid supports has been tested in ozonation attempts.

Granular activated carbon (GAC) can be used as a support for metal oxide immobilization. In spite of a series of drawbacks (fast saturation and need for regeneration or replacement and low efficiency on COD removal), GAC-catalyzed ozonation involves low ozone consumption, owing to the high specific surface areas of the solid supports and its high capacity to generate hydroxyl radicals in the aqueous phase [52].

In the presence of solid catalysts, ozonation is assumed to take place not only in the bulk solution, but also on all the interfaces involved between the different phases present in the reaction mixtures [4,5]. Ozonation on the catalyst surface should prevail, as supported by the significant enhancement when compared to the non-catalyzed process. In this case, the adsorption of at least one reagent turns out to be an essential requirement for the surface reaction and the formation of $\cdot\text{OH}$ radicals.

The ozonation of oxalic acid is an interesting example of oxidative decomposition of refractory organic compound. In this case, a first postulated mechanism is the one involving simultaneously all species adsorbed on the catalyst surface (Scheme 5a). The second reaction pathway (Scheme 5b) proposes a previous dissolution of ozone in the aqueous solution followed by its adsorption from the liquid media onto the solid surface. This is supposed to enrich the catalyst surface with oxidizing species. The consecutive adsorption of the organic molecules will produce their decomposition and possibly the catalyst regeneration by reduction.

Once desorbed, the products of this step will unavoidably be oxidized by $\cdot\text{OH}$ in the bulk solution. In both types of mechanisms, chemisorption of at least one of the reagents is essential, but simultaneous adsorption of two or more substrates should be more beneficial for the ozonation process. The global ozonation process may simultaneously involve both mechanisms and probably other reaction pathways involving diverse adsorbed–adsorbed, adsorbed–dispersed and dispersed–dispersed species interactions. The preponderance of each type of interaction must be strongly dependent on the affinity of the catalyst surface toward a given species, and may vary according to the operating conditions and chemical composition of the reaction mixture. This implies that various interactions between all types of ozone present in the reaction mixture (dispersed gas bubbles, dissolved and adsorbed) with the organic substrates in their adsorbed and (or) soluble forms, along with dispersed hydrophobic clusters (if insoluble) are possible [63]. The high complexity of such a heterogeneous catalytic process is illustrated merely by the high number of direct interactions involving the primary chemical species, i.e., ozone and oxalic acid in the vicinity of a solid surface (Scheme 6).



Scheme 6. Possible direct interactions between the primary ozone species with adsorbed and unadsorbed oxalic acid in the vicinity of a catalyst surface.

This explains why kinetic study of ozonation in the presence of solid catalysts still remains a challenge to be considered. Here, the affinity of the catalyst surface toward ozone, water and (or) the organic substrate is expected to determine the kinetic-controlling step, once the issues related to the low solubility of ozone and the hydrophobic character of the organic substrate in the aqueous media are addressed. The type of solid catalyst must be a key factor when applying ozonation in the decomposition of specific organic molecules.

5. Solid catalysts for ozonation

A wide variety of catalysts have been tested in heterogeneous oxidative processes, as reported by an ample literature [2–96] succinctly illustrated by some attempts summarized in Table 1. A special attention has been focused on dispersed or supported metal oxides, more particularly of titanium, carbon-based materials, zeolites and certain microporous aluminosilicates. Among these, clays minerals are the most abundant in nature, and appear as promising catalysts for such purposes.

Comparison between specific performances of specific pollutant-catalyst-oxidizing systems is quite difficult, and is not targeted in the present work, because of specific operating conditions. However, a deep analysis of the data of Table 1 may be useful to understand the essential requirements for a catalyst to achieve total mineralization of any organic molecules, which remains the main objective of this work.

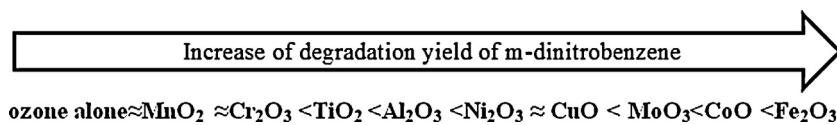
5.1. Metal oxides and metals

MnO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , WO_3 , CuO , CeO_2 , Ni_2O_3 , CoO , V_2O_5 , Cr_2O_3 , MoO_3 , CeO , and $\text{CuO}-\text{CeO}_2$ mixtures represent typical examples of metal oxide catalysts that may exhibit different activities in ozonation processes according to the organic substrate to be oxidized. For instance, Al_2O_3 and MnO_2 were found to produce different decomposition yields with 2-chlorophenol and oxalic acid [30,64]. Conversely, for a given organic substrate such as *m*-dinitrobenzene, extensive studies [54,65] have shown that the catalyst activity in ozonation varies according to the type of the metal oxide used, in the following sequence (Scheme 7).

TiO_2 is a conventional and low cost catalyst widely used in photo-oxidative processes [57], but a growing interest is now focused on new photoactive catalysts such as CdS , ZnS , $\alpha\text{-Fe}_2\text{O}_3$ [38,39,66,67]. Several transition metal oxides and their mixtures such as $\text{Mn}-\text{Ce}-\text{O}$ showed catalytic activity in the ozonation of phenols [61,68]. When separated, unlike cerium oxide, manganese oxide produces complete degradation of oxalic acid after 45 min of ozonation, and showed a constant catalytic activity even after three cycles of oxidation [69].

Table 1
Solid catalysts typically used for oxidation processes.

Catalyst	Organic compound	Oxidation conditions	Cat(g L ⁻¹)	Initial pH	Time(min)	T(°C)	Yield (%)	Ref.
Modified ceramic honeycomb Mn ²⁺ (dispersed) MnO ₂	Nitrobenzene (50 µg L ⁻¹) C.I. reactive red 2 (100 mg L ⁻¹)	C _{ozone} = 1.0 mg L ⁻¹ Ozone: 200 mL min ⁻¹	— 0.1 0.8	6.92 2.0	— 25	25	80 99	[2] [6]
Fe-laponite	Phenol (10 ⁻³ M)	C _{H₂O₂} = 0.05 M	1.0	3.0	—	30	100	[15]
Granulated carbon, carbon black, graphite	Phenol (5 g L ⁻¹)	Oxidation by air	1.0	—	60	20	100	[30]
Hydrotalcite MnO ₂ , Cr ₂ O ₃ , TiO ₂ , Al ₂ O ₃ , Ni ₂ O ₃ , CuO, MoO ₃ , CoO, Fe ₂ O ₃ (10 ⁻³ M)	Phenol (10 ⁻³ M) <i>m</i> -Dinitrobenzene	Ozone: 200 mL h ⁻¹ Ozone: 1.0 L min ⁻¹	1.0 1.0	— 3.0	— 120	20	100 80–100	[50] [54]
Fe ³⁺ exchanged zeolite	Phenol (0.069 M)	C _{H₂O₂} = 0.1 M	0.35	2.5	180	70	77	[61]
Polyamidoxime complexes with Cu, Zn, and Fe	Phenol (10 ⁻³ M)	C _{H₂O₂} = 10 ⁻² M	4.0	9.0	240	25	92, 85, and 87, respectively	[62]
MnO _x /MCM-41 Mn–Ce–O	Nitrobenzene (120 µg L ⁻¹) Phenolics in olive mill wastewater	Ozone: 400 mL min ⁻¹ Mn/Ce ratio: 70/30 Ozone: 500 mL min ⁻¹	1.0 10	6.91 3.4	— 120	15 25	90 91	[63] [68]
MnO ₂	Oxalic acid (10 ⁻³ M)	Ozone: 150 mL min ⁻¹	0.5	3.0	45	—	99	[69]
Nano structured cerium oxide	Oxalic acid (10 ⁻³ M)	C _{ozone} = 50 g m ⁻³ Ozone: 150 mL min ⁻¹	0.15	3.0	180	25	75	[70]
Nano structured cerium oxide	Aniline (10 ⁻³ M)	C _{ozone} = 50 g m ⁻³ Ozone: 150 mL min ⁻¹	0.15	6.0	30	25	100	[70]
Goethite	Phenanthrene (25 ppm)	C _{H₂O₂} = 5 M	33	7.0	720	—	70	[71]
ZnO nanocrystals	Diazinon (20 mg L ⁻¹)	UV lamp 30 W –253.7 nm	0.15	6.5	80	—	80	[72]
ZnO nanocrystals	Phenol (100 mg L ⁻¹)	Ozone: 0.55 mg min ⁻¹	1.25	—	60	25	90	[73]
Carbon nanotube supported MnO ₂	Ciprofloxacin (30.2 µM)	Ozone: 400 mL min ⁻¹ C _{ozone} = 0.40 mg L ⁻¹	1.0	7.0	15	20	89	[74]
TiO ₂ /Al ₂ O ₃ Ratio: 1/9 wt%	Dimethyl phthalate (0.4 mM)	Ozone: 1.95 L min ⁻¹	10	5.6	30	—	100	[75]
Co and Mn doped γ-Fe ₂ O ₃	2,4-Dichlorophenoxyacetic acid (20 mg L ⁻¹)	C _{ozone} = 30 mg L ⁻¹ Ozone: 12 L h ⁻¹ Fe ³⁺ /Co ²⁺ mole ratio = 2	0.8	6.0	—	20	99	[76]
Fe ₂ O ₃ /CeO ₂ on activated carbon	Sulfamethoxazole (100 mg L ⁻¹)	C _{ozone} = 48 mg L ⁻¹ Ozone: 1 L min ⁻¹	2.0	3.0	—	25	100	[83]
Nickel supported activated carbon	p-Chlorobenzoic acid (10 mg L ⁻¹)	Ozone: 50 mg h ⁻¹	5.0	4.31	60	25	100	[84]
Activated carbon supported cerium	Dimethyl phthalate (30 mg L ⁻¹)	Ozone: 50 mg h ⁻¹ Ce amount: 1% w/w	—	5.0	60	25	100	[85]
Cerium oxide	Oxalic acid (10 ⁻³ M)	C _{ozone} = 50 g m ⁻³ Ozone: 150 mL L ⁻¹	0.5	3.0	180	25	85	[86]
MWCNT	Oxalic acid (2.5 × 10 ⁻⁴ M)	Ozone: 480 mL min ⁻¹ C _{ozone} = 20 mg L ⁻¹	0.1	3.0	40	20	80	[87]
Fe/SBA-15	Dimethyl phthalate (10 mg L ⁻¹)	C _{ozone} = 50 mg L ⁻¹ Ozone: 0.8 L min ⁻¹	0.2	5.7	60	25	100	[90]
Fe/MCM-41 0.5% w/w Fe	p-Chlorobenzoic acid (10 mg L ⁻¹)	Ozone: 1.2 L min ⁻¹	1.0	4.3	20	25	100	[91]
Co–Mn–Al	Nitrobenzene (10 ⁻⁵ M)	C _{ozone} = 100 mg L ⁻¹ C _{ozone} = 0.41 mg L ⁻¹ Ozone: 400 mL min ⁻¹ Co/Mn/Al ratio: 4/2.13/0	0.5	6.99	10	19	60	[96]



Scheme 7. Variation of the catalytic activity versus the metal oxides in the degradation of *m*-dinitrobenzene.

These differences in catalytic activity can be partly explained by the specific features of the catalyst surface, more particularly the acid-base properties of each catalyst, which must play a key-role in the adsorption of the reagents. For instance, moderately acidic surfaces such as clay-supported metal cations were found to produce appreciable degradation yields of oxalic acid due to a synergy between adsorption and the catalytic activity of the exchangeable cations [59]. The latter may act on the catalyst surface and (or) in the bulk solution, according to its mobility in the vicinity of the catalyst surface, which strongly depends on the pH level of the reaction mixture. Similar synergy was also noticed for nano-structured cerium oxide catalysts [70].

Effective adsorption supposes high specific surface area, which usually requires increased porosity and (or) high catalyst amount. However, high ozonation levels require optimum catalyst quantities in correlation with adequate pH levels, as supported by the complete mineralization of phenanthrene on goethite at pH 7.2 [47,71], of oxalic acid on iron-exchanged montmorillonite at pH 3.0–3.5 [59] or of the diazinon insecticide on ZnO nanocrystals at pH 5.2.

Under similar operating conditions, the catalyst characteristics play a key-role even in the case of almost similar structures. For instance, ZnO nanoparticles showed higher efficiency in phenol ozonation, as compared to manganese and cerium mixed oxides [72,73]. This was partly explained in terms of higher surface area, the other contribution being attributed to the metal characteristics. The dispersion state of metal oxides does not seem to play a significant role, inasmuch as both dispersed manganese oxide and carbon-supported manganese oxides showed high catalytic activities at acidic pH, which is supposed to involve mainly the action of molecular ozone [74]. In some ozonation processes, metals appear to exhibit higher catalytic activity in their cationic form, as supported by the higher ozonation efficiency in the presence of Mn²⁺ as compared to MnO₂, more particularly at pH 2 [6]. This was explained by the involvement of molecular ozone attack, presumably due to an enhancement of the direct interaction with more mobile and available cations in acidic media as a result of partial metal oxide dissolution in acid media.

This explains that, notwithstanding its apparently lower effectiveness, MnO₂ is still tested in the ozonation in controlled acidic media of a wide variety of organic substrates such as oxalic acid, pyruvic acid, sulfosalicylic acid, propionic acid, glyoxalic acid and phenol. TiO₂-supported MnO₂, FeOOH and SnO₂, brucite and magnesia, magnetic cobalt and Mn-doped γ-Fe₂O₃, granular activated carbon have also been tested as catalysts in ozonation processes [75–77]. The growing interest devoted to metal oxides resides, thus, in their ability to act as a cation sources in moderately acidic pH through partial dissolution. Nevertheless, even though metal cations are supposed to act as the main catalytic species, many aspects related to their mechanism pathways still remain to be elucidated.

Solids may also be used as supports for catalysts. In this regard, except organic solids such as polymers and dendrimers, which are known to be highly reactive toward ozone, all kinds of materials that exhibit sufficiently high stability against irreversible oxidative decomposition can be used as catalyst supports. So far, a wide variety of inorganic supports such as zeolites, clay minerals, silica gel, Al₂O₃ or TiO₂ has been used for this purpose [5]. Zeolite and

alumina showed the lowest catalytic activities [5,78,79]. For instance, TiO₂/Fe²⁺ and TiO₂/Fe³⁺ turned out to be interesting catalysts for the oxidative decomposition of many organic pollutants. Alumina-supported TiO₂ or Fe₂O₃ have been employed for removing oxalic acid, chloroethanol and chlorophenol from water [80], or fulvic acid from wastewater [81]. Ruthenium and cerium oxides have been tested for succinic acid removal [5]. Reportedly, supported noble metals such as Pt/TiO₂ and Pt/Al₂O₃ can produce total decomposition of organic compounds [61]. Ru/CeO₂ systems appear to produce complete removal of succinic acid from wastewater after only 60 min [82], taking into account that total decomposition of most organic contaminants still remains a difficult challenge to achieve.

5.2. Carbon-based catalysts

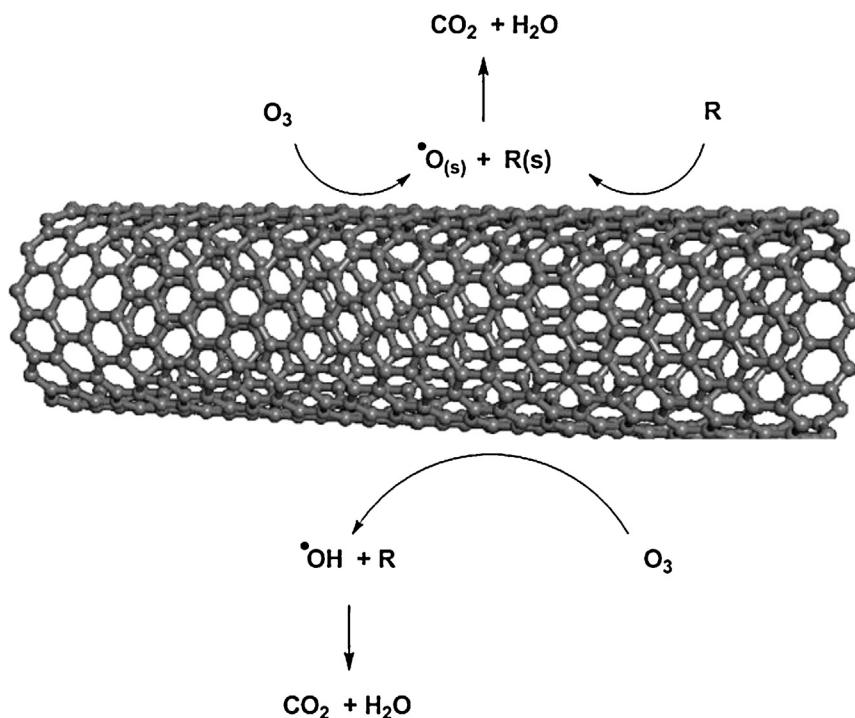
These last years, many types of carbon based structures have been tested as catalysts or supports in oxidative processes, and have produced more or less satisfactory results in the decomposition of a wide variety of organic molecules. Indeed, granulated activated carbon (GAC), carbon black powder and graphite have been employed as catalysts or catalyst supports for Pt, Pd, Ru in the oxidation of phenols and halogenated phenols, carboxylic acids such as acrylic, acetic, formic, oxalic, succinic, adipic, propionic, glutaric, and butyric acid [30]. Fe₂O₃ and CeO₂ immobilized on activated carbon turned out to be effective catalysts in the ozonation of antibiotics [83]. Activated carbon-supported nickel showed significant catalytic activity in the ozonation of *p*-chlorobenzoic acid as compared to non-catalytic processes [84].

Ozone-granulated activated carbon (O₃/GAC) is a typical example of catalytic ozonation, which produces thorough degradation of pesticides [9,54]. In the oxidation of oxalic acid, cerium oxide showed lower activity than its carbon-supported counterpart [85]. Here, the specific surface area and metal oxide particle diameter are supposed to play key roles [86]. Another interesting carbon-based structure is the so-called multiwalled carbon nano tubes (MWCNTs), and consists in mesoporous nano materials with linear channels. Reportedly, oxidation attempts using such materials resulted in exhaustive phenol decomposition [61], with interesting behavior toward refractory intermediates such as oxalic acid [87]. As many types of solid catalysts, MWCNTs appear to act as initiators for surface bound oxidative species (**Scheme 8**).

On such materials, oxidations of organic molecules were found to take place not only in the bulk solution but at the catalyst surface as well [65]. The general tendency is that, the use of solid catalysts is beneficial, because the global oxidation process often involves a complementary contribution of the surface adsorption steps. Such enhanced oxidation processes may lead to complete mineralization of the organic molecules. This implies that the extent of the specific surface areas should play a key role as in any solid-fluid interface processes, and that expanded structures having high surface-to-bulk ratio should be strongly recommended catalysts or catalyst supports for this purpose. Aluminosilicates such zeolites, clays and clay minerals must be very interesting in this regard.

5.3. Zeolites and related catalysts

Aluminosilicate family includes a wide variety of amorphous and crystalline phyllosilicates such as clays and clay minerals,



Scheme 8. Schematic representation of possible interactions for oxalic acid (R) ozonation on MWCNTs.

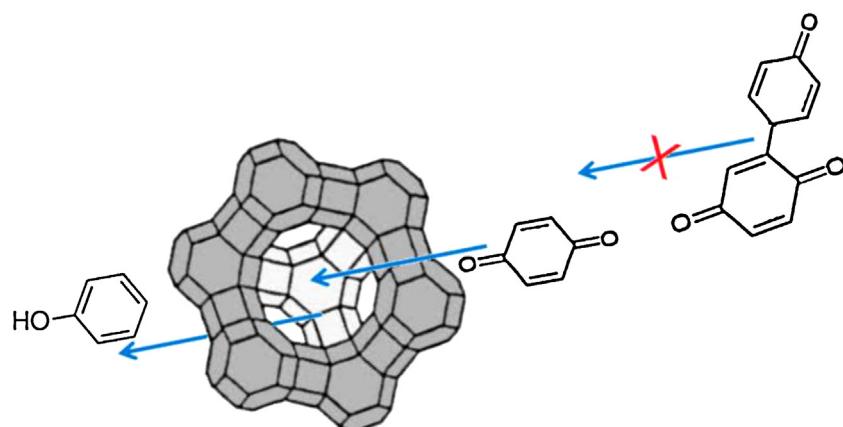
and tectosilicates such as zeolites. The common feature of all these structures resides in the occurrence of permanent negative charges arising from the replacement of $[SiO_4]^{4-}$ tetrahedra by $[AlO_4]^{3-}$ anions. These charges can be compensated by cations usually belonging to alkali and alkaline earth metals. Aluminosilicates are solid acids, which have been used as catalysts in many chemical processes.

Zeolites are crystalline and microporous aluminosilicates than can offer high specific surface areas for adsorption and catalysis. Such structures have 3-D frameworks with channels and cavities that can allow diffusion of a wide variety of organic molecules with critical diameter around that of monoaromatic hydrocarbons, such as benzene, toluene, xylene, and other monoaromatic derivatives (Scheme 9).

They have already been tested as catalysts in the ozonation of organic molecules. Seemingly, this oxidation reaction is related to

ozone interaction with Lewis acids on the zeolite surface, and an increase in surface acidity through suitable modifications enhance the process efficiency [88]. Ferric ions are well known to exhibit a special capacity for decomposing organic molecules in the presence of oxidizing agents, and an ample literature is available in this regard. Fe^{2+} ions exchanged zeolites were also found to display the highest effectiveness, by achieving almost total removal of organic pollutants from certain wastewaters [61].

Pseudo-zeolites are similar to zeolites with crystalline 3-D frameworks built with cavities and interconnected channels. Mesoporous silicas like MCM and SBA series are not aluminosilicates, and rather regarded as being pseudo-zeolites. Such materials can host a wide variety of organic molecules with less size constraints as compared to zeolites. Some of these materials, such as MCM-41, produced appreciable toluene removal with yields reaching of up to 96% from contaminated wastewaters [89]. The general tendency is that MCM-41 showed higher effectiveness in ozonation



Scheme 9. Molecular sieving property of zeolites. Here, as an example, phenol and *p*-benzoquinone can diffuse freely across the zeolite channels and cavities, unlike bulkier molecules.

attempts as compared to zeolites, most likely due to their higher specific surface areas ($975\text{ m}^2\text{ g}^{-1}$ versus $530\text{ m}^2\text{ g}^{-1}$).

Reportedly, mesoporous $\text{Fe}^{3+}/\text{SBA-15}$ silica produced total decomposition of dimethyl phthalate through ozonation at pH 5.7. However, such a performance accounts for only 35% removal yield of total organic compounds (TOC), providing clear evidence that no thorough mineralization into CO_2 took place. Raising pH up to 9.0 was found to produce a slight enhancement in TOC removal, suggesting an $\cdot\text{OH}$ radical mechanism. This is supported by the detrimental effect produced by the addition of $\cdot\text{OH}$ radical scavengers [87]. On such materials, excessive amounts of cations and anions seem to affect the overall SBA-15 activity [90]. $\text{Fe}/\text{MCM-41}$ showed appreciable catalytic activity in the ozonation of *p*-chlorobenzoic acid in aqueous media, affording TOC removal yields of more than 94.5% after 60 min of oxidation. Under similar conditions, the TOC removal yields were only 61.5% on MCM-41 and 62.3% without catalyst. Here also, such a process seems to occur via $\cdot\text{OH}$ mechanism pathway. Seemingly, the catalyst effectiveness is maximum for an optimum iron amount of 0.5% [91]. Similar phenomenon was observed on MnO_2 supported on mesoporous silica ($\text{MnO}_2/\text{MCM-41}$). Such catalysts produced nitrobenzene oxidation yields of up to 93.3% after 10 min of ozonation in the presence of an optimum MnO_2 concentration of 1.15% [63].

5.4. Mixed hydroxide catalysts

Layered double hydroxides (LDH) are anionic clay minerals, which have also been used as ozonation catalysts. In this regard, $\text{Co}-\text{Mn}-\text{Al}-\text{LDH}$ in different Co/Mn ratios have been tested in the ozonation of nitrobenzene, and $\text{Co}_4\text{Mn}_2-\text{Al}-\text{LDH}$ sample was found to produce the highest degradation yield of 60% at pH 6.99 and at room temperature [96]. Interestingly, the yields of mineralization into CO_2 did not exceed 20% with the same catalyst under similar conditions, indicating the formation of large quantities of intermediates. This appears to be a common feature of many LDH-based catalysts, and a possible explanation is the surface basicity that might not favor adsorption like under acidic media. As a confirmation in this observation, deeper insights showed that increasing cobalt amounts enhance the catalytic activity.

In contrast, increasing Al concentrations were found to be detrimental, presumably due to an enhancement of the surface basicity [59]. Reportedly, hydrotalcite, which consists of $\text{Al}-\text{Mg}-\text{LDH}$ materials, has been tested in phenol oxidation [61], but, seemingly higher performance in the catalytic ozonation of phenol and oxalic acid in water was registered when used as a support for metal oxides such as CuO [50]. Total disappearance of phenol was measured after less than 30 min and total mineralization of oxalic acid was obtained upon 210 min of catalytic ozonation. Such a performance still remains, by far, below those registered with cationic clay minerals. Performance comparison is difficult, because different catalyst-pollutant systems require different operating conditions, but may be useful for understanding the main approaches in this research area.

Ferral is a natural material composed of aluminum sulfate, ferric sulfate, ferric oxide, aluminum oxide and magnesium oxide. Reportedly, high decomposition yields of organic dyes of up to 99% were obtained through wastewater ozonation at acidic pH's [97]. Here, the mere presence of Fe cations, most likely due to partial dissolution of the material, seems to play a key role in the catalytic activity of such material. Thus, it clearly appears that free metal cations in the vicinity of a solid surface is an essential requirement for enhancing interaction with all the ozone forms present in the reaction mixture.

Among the wide variety of solid catalysts tested so far, only aluminosilicates, and more particularly clay minerals, appear to fulfill this requirement that favors cation mobility and catalytic

activity. Interesting and low cost aluminosilicates are those belonging to the smectite clay mineral family, more specifically montmorillonite, the main component of bentonites. A special interest is now devoted to this clay mineral due to its high surface area of up $200\text{ m}^2\text{ g}^{-1}$ and even beyond through suitable modification procedures, increased cation exchange capacity, higher adsorption and swelling capacity as compared to other counterparts.

5.5. Clays, clay minerals and montmorillonite

Unlike zeolites, clay minerals are dispersed crystalline frameworks, most of them having layered structures but almost similar surface properties as zeolites. Their wide abundance in nature makes them to be regarded as low cost alternatives to zeolites in many applications. There exist various types of clays, which are natural raw mixtures of clay minerals, volcanic ashes, silicas, carbonates, and miscellaneous. One of the most representative clays is bentonite and one of the most studied clay mineral is montmorillonite [92]. Bentonite is a clay material mainly composed by smectite and other minerals like feldspar, biotite, quartz, pyroxenes, and zircon [93]. Smectite is a family of several minerals such as montmorillonite, saponite, vermiculite, nontronite, hectorite, volkonskoite, saucinite, and beidellite. Kaolinite is also another clay family that differs from smectites by the layer number and arrangements.

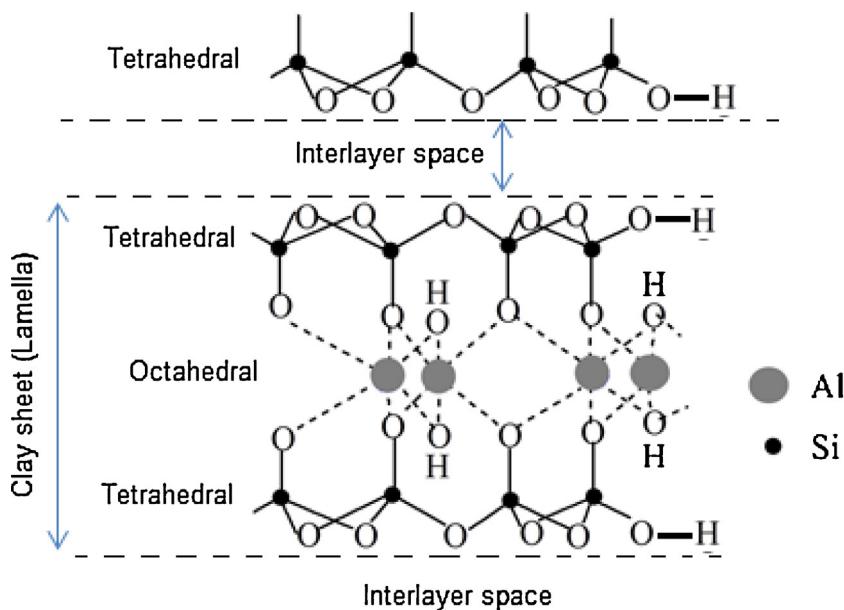
Many examples of clay-catalyzed oxidation processes at room temperature have been reported in the literature. $\text{Al}-\text{Fe}$ pillared clays ($\text{Al}-\text{Fe}$ PILCs) were found to display improved catalytic activity toward phenol oxidation at moderately acidic pH values [15,94]. Cu-doped alumina-pillared montmorillonite has been successfully used for oxidation of toluene and xylene [6,95]. Phenol oxidation has also been tested on metal-exchanged clays and pillared clays [61]. ($\text{Al}-\text{Fe}$)-PILC showed the highest performance, affording removal yields of up to 100%.

Attapulgite-based catalysts were reported to improve TOC removal by approximately 20% as compared to the non-catalytic ozonation [5]. Reportedly, Fe-doped laponite produced total removal of phenolic compounds, antibiotics and azo-dyes from wastewaters [15]. Ceramic honeycomb modified by impregnation of metals such as Mn and Cu gave conversion yield of about 80% in the ozonation of aqueous solutions of nitrobenzene. This conversion yield is three times higher than that of non-catalytic ozonation [2].

Montmorillonite is probably one of the most studied clay mineral [92], whose surface properties can be significantly improved through simple procedures, providing effective materials for adsorption and catalysis [98,99], more particularly in oxidation reactions [100–102]. The structure of each montmorillonite sheet consists of a layer of octahedral alumina [$\text{Al}_2(\text{OH})_6$] sandwiched between two layers of tetrahedral silicates [$\text{SiO}_4]^{4-}$ (Scheme 10).

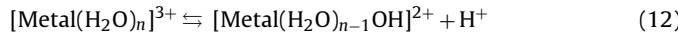
In the presence of water molecules, the interlayer spacing enlarges, inducing clay swelling that facilitates exchange of the interlayer cations, usually Na^+ , Ca^{2+} and Mg^{2+} . The surface negative charges originate from isomorphous substitution of Al^{3+} by Mg^{2+} species in the structure of the octahedral layer. In dry montmorillonite, the exchangeable cations are located within the hexagonal cavities of the silica layer, but upon hydration, the cations move into the interlayer spacing [98].

The strength distribution of the acid sites can be modified by ion-exchange, dealumination through acid attack or incorporation of alien molecules or particles. Incorporation of heavier metal cations displaying high solvation capacity is known to generate Brønsted and Lewis acid sites. The Brønsted acidity originates from the



Scheme 10. Structure of montmorillonite.

dissociation of the intercalated water molecules coordinated to cations, as illustrated by Reaction (12):



Heating up to 200–300 °C is known to induce a decrease in the Brønsted acidity but an increase in Lewis acidity. Excessive heating to around 450 °C and above usually results in complete dehydroxylation of the aluminosilicate lattice and a thorough conversion of Brønsted acid sites into Lewis acidity.

An additional feature of montmorillonite resides in its double-faced lamella structure. The latter offers twice its capacity to retain both adsorbed and dispersed metal cations in the vicinity of the solid surface. Moderately acidic pH was already found to favor weak ion-exchange by proton, providing, thereby, sufficient released cation that can also interact with unadsorbed molecules of ozone and organic substrate [22,59,60]. Besides, both faces of montmorillonite lamellae possess sufficient electrostatic charges that improve the adsorption capacity. The solid surface can attract and concentrate not only the organic substrate molecules, but also ozone in both adsorbed and dissolved forms, along with dispersed micro-bubbles (Scheme 11).

High catalytic activity requires high number of available clay sheets devoid of dense silica phases that do not contribute to the above mentioned surface processes. In some cases, clay mineral purification turns out to be necessary for ozonation processes, because the presence of some impurities such as carbonates, bicarbonates, and organic materials may affect ozone efficiency. In oxidative processes, carbonates and bicarbonates are known to act as radical scavengers, while organic components involve undesired competitive ozonation processes that impose additional ozone amounts. Convenient and effective purification of montmorillonite involves full ion-exchange into the desired homo-ionic form, combined with a selective sedimentation in water under ultrasound exposure and removal of the lower fractions that contains various ashes, dense phases like quartz, and other impurities. Purification may be completed by either ozone bubbling at room temperature or controlled calcination up to 400–450 °C to remove possible carbonates and (or) organic impurities. Heating can be avoided by ozone treatment for removing organic impurities and slight leaching by impregnation in diluted acid solutions for carbonate elimination. The final step involves dialysis in water in order to

remove the excess salt resulting from ion-exchange [92]. In most cases, montmorillonite-based catalysts are prepared starting from the Na⁺ exchanged (NaMt) [92,103–105]. All these purification steps do not use organic solvent, and are fairly easy to carry out in water at ambient temperature and pressure.

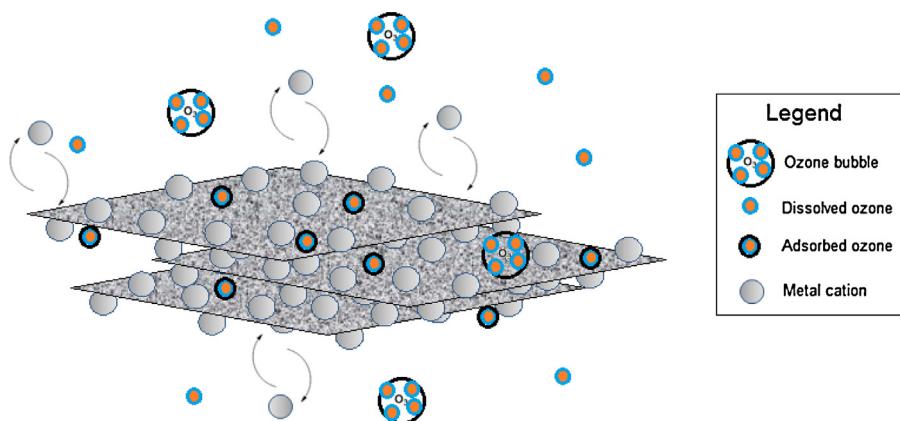
6. Key parameters in catalytic oxidative processes

6.1. Catalyst amount and lifetime

Ozone appears as being the most convenient oxidizing agent in terms of production, handling and consumption constraints, as supported by an ample literature in this regard. Indeed, even in the absence of catalyst, cost comparison showed that ozonation is much more effective in terms of reaction time than photochemical and Fenton oxidative processes or even than adsorption on granulated active carbon in dimethylphenol elimination [1]. Under similar common conditions, the required time for total decomposition of dimethylphenol by Fenton process was of 35 min, but of only 13 min through ozonation in acidic medium and 7 min in alkaline medium. The required amount of oxidizing species (H₂O₂) in Fenton process is 680 mg L⁻¹, while ozone doses of only 13 and 25 mg L⁻¹ are needed in alkaline and acidic media, respectively [1]. In all cases, the use of optimum catalyst concentrations was found to modify favorably the reaction mechanisms toward an improvement of the process efficiency [53] and an increase of the quantities of the oxidizing species [53,62,106,107].

This allows envisaging large-scale facility implementations, notwithstanding that research is still in progress throughout the world to produce high performance catalysts for achieving total mineralization of organic contaminants, when required, with minimum ozone consumption. The required catalyst quantity depends on its very chemical structure and that of the organic molecules to be eliminated. For instance, ozonation requires an optimum concentration of CuS-based catalyst of 400 mg L⁻¹ for treating textile dye-containing waters [53], but of 500 mg L⁻¹ of ZnO nanoparticles for the decomposition of dichloroacetic acid [108]. Municipal sewage treatment can be efficiently achieved with only 70 mg L⁻¹ of TiO₂ [38].

In radical mechanism pathways, like that involved in Fenton processes, the optimum amount of free Fe²⁺ cations needed was



Scheme 11. Metal cation mobility and ozone concentration in the vicinity of homo-ionic form of montmorillonite surface.

explained by the occurrence of scavenging reactions between these ions and hydroxyl radicals [3,109]. When using ash-supported Fe²⁺ cations, the detrimental effect of excessive catalyst amounts with respect to the optimum value may be explained in terms of reduced contact surface through particle aggregation into clusters [44]. In clay minerals [22,59,60], such a phenomenon was attributed to the fact that high catalyst concentrations enhance clay–clay interactions at the expense of those occurring between clay lamella and ozone and (or) the organic substrates.

In oxidation processes, the effectiveness of solid catalysts is expected to decrease in time with increasing number of reuses [38,110]. In some cases, this must be due to unavoidable alteration by leaching of the catalyst surface, more particularly in excessively acidic or alkaline media. Leaching is often observed in ion-exchanged catalysts such as zeolites and clay minerals. On hybrid organic–inorganic catalysts such as metal-containing polyamidoxime grafted on starch, the activity decay was explained by a possible accumulation of the reaction products on the organic moiety [62]. Nonetheless, the authors of this work did not emphasize on the possible oxidative decomposition of the organic moiety of the solid catalyst.

For aluminosilicates such as clay minerals, cation losses, even in moderately acidic media, were already reported [22,59,60]. Improvement attempts have suggested catalyst refreshing through periodical ion-exchange treatments for maintaining the catalytic activity for more than fifty cycles [60]. Such a treatment targets a re-saturation of the exchangeable sites with metal cations. Investigations are still in progress in this regard.

In many cases, slight heating, more particularly between 10 °C and 20 °C, was found to enhance the catalytic activity in oxidative degradation processes of organic molecules [3,15,53,62,107]. This was usually explained in terms of an acceleration of the reactions that generate •OH radicals [62]. However, in some cases, excessive temperature increase is expected to produce detrimental effects, by reducing the ozone solubility in water. This explains why, in most cases, room temperature is regarded as being optimum, more particularly for catalytic ozonation [5,22,59,60,110]. Similar observations were made when performing the ozonation of dimethyl phthalate over Fe/SBA-15 [90], of p-chlorobenzoic acid over Fe/MCM-41 catalyst [91], or of oxalic acid on MWCNTs [87]. Nevertheless, such a detrimental effect of temperatures higher than the ambient values may also be explained by a possible acceleration of the decomposition of radical species, if any, or by an attenuation of reagent adsorption on the surface of the solid catalyst [60]. Besides, higher temperatures may also produce undesired pH modification constraints for process monitoring.

6.2. Correlation between catalysts and pH

In processes involving oxidizing agents and more particularly radicals, the pH level of the reaction mixture is expected to strongly influence the mechanisms pathways [59,60]. High pH's are known to promote the formation of hydroxyl radicals. This is supported by an ample literature on a wide variety of oxidation processes, more particularly in the ozonation of phenol on activated carbon [111] and on starch-supported metal-containing polyamidoxime [62], or in the oxidative elimination of methylene blue on zeolite [88].

In the ozonation of dichloroacetic acid on ZnO nanoparticles, alkaline pH's were found to produce much higher degradation yields, due the formation of negatively charged ZnO[−] species, as compared to pH 2, which gave oxidation yields ca. 6 times lower [108]. The detrimental effect of low pH was explained in terms of a predominance of scavenging effect of H⁺ ions on the low quantities of hydroxyl radicals produced in acidic media. Additional arguments in this regard are provided by attempts in the photocatalytic oxidation of organic compounds [38]. For instance, when using TiO₂ as catalyst, high degradation yields were obtained under conditions favoring the production of hydroxyl radicals [106]. The catalytic ozonation of nitrobenzene on ceramic honeycomb produced almost total decomposition after 10 min at pH 9. At acidic pH values, the degradation yields did not exceed 20% [110]. However, alkaline pH's may also cause detrimental changes in the structure of some catalyst surfaces mainly through precipitation processes, as observed for ion-exchanged montmorillonite [59].

In the presence of supported cations [15], a Fenton-like catalytic oxidation produced an almost total decomposition of phenol at acidic pH of 2.5–3.0. Such pH levels are supposed to promote the production of oxonium ions (H₃O⁺) [3]. However, at acidic pH's, care should be taken to prevent catalyst decomposition, more particularly when using aluminosilicates, which may undergo dealumination. In moderately acidic pH's around 3, appreciable decomposition yields are also possible, as observed in the photocatalytic ozonation of pyrrole-2-carboxylic acid [57] and the catalytic ozonation of p-chlorobenzoic acid and phenanthrene on ferric oxyhydroxide (FeOOH) [47]. As previously stated for ozonation in the presence of ion-exchanged montmorillonite [22,59,60], intermediate pH values ranging from 2.5 to 4.5 appear to involve a synergistic effect between adsorption and oxidation, and between ozonation on the catalyst surface and in bulk solution.

In most cases, the oxidizing capacity of ozone is considerably attenuated and sometimes even suppressed at neutral pH's. For certain catalysts, pH values around neutral produced the lowest activity regardless to the catalyst used [38,60]. This must be due to the occurrence of a pH threshold with changes in the

mechanism pathways. Around pH 6–8, the reactive and catalytic species involved in both acidic and alkaline pH's must display the lowest concentrations in the reaction mixtures. Under these conditions, any slight pH change may produce pronounced detrimental interactions between the species present in small amounts in the liquid media. In all cases, changes in pH's unavoidably take place during oxidation reactions, due to the formation of intermediates and accumulation of short-chain carboxylic acids [7,68,112]. This explains somehow, and at least partly, the decay in time of the catalytic activity during most oxidation process supposed to be favored by moderately acidic pH's.

The effect of pH variations should be strongly correlated to the presence and structures of the catalysts employed. These pH changes may be enhanced by the presence of catalyst, which, in turn, may undergo modifications in both chemical composition and surface properties. Such modifications are specific to each type of catalyst. For instance, the non-catalytic ozonation of textile dyes showed high efficiency at alkaline pH's, due to the production of hydroxyl radicals, but this performance shifts to moderately acidic pH's when using CuS as catalyst [113].

This clearly indicates that non catalytic ozonation does not proceed via the same pathway as in the presence of catalyst, and that the concept of optimum pH for high radical production, if any, is specific to each type of catalysts [53]. For instance, volcanic sand acted as effective catalyst in the ozonation of benzothiazole at pH 7, due to the predominant contribution of a radical mechanism [114]. Effective radical mechanisms seem to be involved at pH 10 in the ozonation of aromatic compounds in the presence of porous manganese and cobalt-modified diatomaceous materials [115], but only at pH 4 in the catalytic ozonation of molasses on SnO₂ [116]. On solid catalysts, the optimum pH values should be correlated to the acid-base interaction between the catalyst surface and the dispersed species. Here, the concentrations of ozone [52] and of the organic substrates [53] along with the very acid-base properties of the catalyst surfaces and of the organic species [59,88] must play significant roles, more particularly in reagent adsorption. Elucidation of the roles of acid-base interactions between all the species dispersed in the liquid media imposes intensive investigations in this regard.

7. Conclusion

The data examined in this review allow concluding that effective water treatments without traces of persistent hazardous by-products or toxins can be achieved through suitable oxidative processes. The results obtained after intensive research have succeeded in imposing a new ecologic vision in designing complete oxidative treatments of wastewaters. In this regard, the total absence of any traces of organic by-products has progressively become a major issue to be addressed. In other words, a wide variety of catalysts is now studied for improving oxidative degradations of organic contaminants in aqueous media. All these studies has focused their interest toward thorough mineralization into inorganic final products that can be released in the environment (CO₂ and water), easily removed by dissolution in water (SO_x, NO_x and derivatives) or retreated into added-value derivatives. Nevertheless, notwithstanding the outstanding achievements made in wastewater treatments, the total removal of organic contaminants with low energy consumption and without generating traces of persistent toxins still remains a challenge difficult to achieve. This is mainly due to the refractory character toward oxidation of short chain derivatives, more particularly oxygenated compounds.

The data summarized herein show that, among all the research directions undertaken so far, those targeting the improvements of oxidative procedures, more particularly ozonation, are

probably the most promising routes for economical, technological, and ecological reasons. Some of these procedures, and most specifically solid-catalyzed ozonations under optimum conditions, have already made possible not only the total decomposition of organic compounds containing only hydrogen, carbon, and oxygen atoms, but also the total mineralization of their by-products into carbon dioxide. A key-step in achieving such a performance resides in the rigorous choices of adequate solid catalysts to be used in optimum amount under optimum pH conditions, in correlation with the nature of the organic substrates to be decomposed. All these factors are supposed to produce a synergy in promoting suitable mechanism pathways that involve both adsorption and surface reaction for the oxidative degradation of a given organic substrate.

There are no common rules in adopting alkaline or acidic pH's for wastewater treatments. However, a deep analysis of the data examined allows stating that solid catalysts with ion exchange capacity are supposed to promote ozonation both on the catalyst surface and in the bulk solution in moderately acidic media. The oxidative techniques, including the catalyst types and concentrations and all the other parameters discussed herein should be selected according to the contaminant's nature and the acid-base properties of every wastewater to be treated. For economic reasons, crystalline aluminosilicates and more particularly clay minerals appear as promising catalyst supports for such purposes. Through judicious and convenient modifications, their acid-base properties, adsorption capacity, affinity toward reagents and others can be willingly modulated for specific applications in the treatment of specific organic contaminants in specific wastewaters. This possibility to control the clay mineral catalytic activity opens new prospects in wastewater treatments for producing clean waters without any traces of harmful and toxic derivatives.

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